

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
8 February 2001 (08.02.2001)

PCT

(10) International Publication Number
WO 01/08785 A1

(51) International Patent Classification⁷: **B01D 53/34, 53/50, 53/56, 53/60**

(21) International Application Number: **PCT/US00/20518**

(22) International Filing Date: **27 July 2000 (27.07.2000)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
09/363,912 28 July 1999 (28.07.1999) US

(71) Applicant: **THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION [US/US]; 1960 Kenny Road, Columbus, OH 43210-1063 (US).**

(72) Inventors: **FAN, Liang-Shih; 2153 Shawnmont Court, Dublin, OH 43016 (US). AGNIHOTRI, Rajeev; 140 West 19th Avenue, Columbus, OH 43210 (US).**

(74) Agent: **GILCREST, Roger, A.; Standley & Gilcrest LLP, Suite 210, 495 Metro Place South, Dublin, OH 43017 (US).**

(81) Designated States (national): **AU, CA, CN, JP.**

(84) Designated States (regional): **European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).**

Published:
— *With international search report.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/08785 A1

(54) Title: **CARBONATION ASH REACTIVATION PROCESS AND SYSTEM FOR COMBINED SO_x AND NO_x REMOVAL**

(57) **Abstract:** The present invention includes methods and apparatus useful in the removal of air pollutants (SO_x and NO_x) and trace toxins from coal-fired combustors. A coal-fired combustor may be retrofitted to accommodate combined SO_x/NO_x removal technology for solid waste reduction and environmentally responsible utilization of dry flue gas desulfurization (FGD) product. The combined SO_x/NO_x control technology may integrate enhanced removal of SO₂ at high to medium temperatures using a desulfurization process of the present invention with selective catalytic reduction technology for NO_x. The reactivation of spent sorbent and dry FGD product may result in a more complete utilization of the ash and sorbent in the reduction of SO₂ emissions, thereby reducing significantly the amount of sorbent used and the volume of by-product generated.

CARBONATION ASH REACTIVATION PROCESS AND SYSTEM
FOR COMBINED SO_x AND NO_x REMOVAL

5 Technical Field of the Invention

The present invention is in the field of pollution and contaminant removal.

Background of the Invention

This invention relates to apparatus useful in the removal of air pollutants. More specifically, this invention relates to apparatus useful in mitigating major air pollutants (i.e., 10 SO_x and NO_x) and trace toxins from coal-fired combustors.

The residual solids resulting from various flue gas desulfurization (FGD) processes, including scrubber sludge, contain significant portions of unreacted sorbent. Unless these solids are treated, they will be sent to landfills, thus increasing the cost associated with 15 sorbent requirements and waste disposal.

15 Nitrogen oxides (NO_x) are emitted when fossil fuels such as coal, natural gas, or oil are burned in air. NO_x emissions have attracted increased attention in recent years as more is learned about their role in acid rain, smog, visibility impairment and global climate change. About half of all nationwide NO_x pollutants come from automobiles, whereas coal-burning utility boilers contribute about 25% of the total. The 1990 Clean Air Act amendments require 20 all coal-fired utility boilers over a certain size to reduce NO_x by about 50%. In addition, it is expected that regulations affecting the emission of NO_x will get tougher in the future and power plants will need to reduce emissions even further. Another serious problem may occur in integration, when trace metals and NO_x may contaminate the catalyst.

In coal-fired power plants, disposal of coal combustion products such as ashes and 25 wet/dry FGD products is a serious concern. Most of these solid wastes are sent to landfills for

disposal. Studies have shown that, when treated properly, these solid waste products can be used beneficially in a number of applications.

It is therefore an object of the invention to provide a cost-effective method and apparatus for reducing the residual solids produced during the mitigation of major air 5 pollutants and trace toxins from coal-fired combustors by recycling the unreacted sorbent contained in those solids.

Although described with respect to the field of mitigating major air and trace toxins from coal-fired combustors, it will be appreciated that similar advantages may obtain in other 10 applications of the present invention. Such advantages may become apparent to one of ordinary skill in the art, in light of the present disclosure or through practice of the invention.

Summary of the Invention

The present invention includes a reactivation technique developed from a fundamental understanding of the pore structural properties of both CaCO_3 and $\text{Ca}(\text{OH})_2$, and the 15 evolution of pore structure with calcination and sintering.

Integration of a SO_x removal process of the present invention with SCR technology for NO_x removal offers an attractive alternative to post-combustion flue gas clean-up technologies as it not only reduces the emission of acidic pollutants but also reduces the amount of solid-waste generated. The combined SO_x/NO_x technology of the present invention 20 integrates a novel ash reactivation process for SO_x removal with proven SCR technology for NO_x removal. The coal fired power plants that use high sulfur coals can be encouraged to continue using these coals by retrofitting to include the inventive process for advanced, cost effective NO_x and SO_2 removal combined with reduced solid waste generation and increased dry FGD product utilization.

A recycling of spent sorbent and fly ash mixture into the spray dryer may result in substantial improvements in reagent utilization and SO₂ removal. Substantial reactions may occur between the fresh Ca(OH)₂ and recycled fly ash from spray dryer, resulting in the formation of hydrated calcium silicates. Their subsequent reaction with SO₂ may lead to 5 increased efficiency. The recycling of used sorbents is described in co-pending application Serial Number 09/073.237, which is hereby incorporated herein by reference.

Although not limited to the theory of the invention, the key to the high reactivity of a fresh or partially utilized sorbent may lie in its open initial internal structure and subsequent pore structure evolution under high temperature conditions. The present reactivation 10 technique may be used for spent and under-utilized sorbents, and benefits from the pore structural properties of both CaCO₃ and Ca(OH)₂, and the evolution of pore structure with calcination and sintering. The present invention includes a suspension-based carbonation process in which the unreacted CaO is converted into calcium carbonate (CaCO₃) instead of calcium hydroxide (Ca(OH)₂).

15 Along with reactivation of unreacted CaO, this process provides a better distribution/exposure of available calcium than the reactivated spent sorbent from hydration alone. The process of the present invention has been successfully applied to the reactivation of two partially utilized sorbents generated in the laboratory, and has been further demonstrated to reactivate two commercial ash samples under bench-scale conditions.

20 Accordingly, the present invention includes devices and systems useful in removing air pollutants. This invention also includes machines or instruments using these aspects of the invention. The present invention may be used to upgrade or retrofit existing machines or instruments using methods and components known in the art.

The present invention also includes methods and processes using the devices of the present invention. The methods and processes of the present invention may be applied using procedures and protocols known and used in the arts to which they pertain.

In broadest terms, the present invention includes a method of removing SO_x and trace metals from a gaseous waste stream from coal combustion, where the coal combustion generates an untreated gaseous waste stream containing SO_x and trace metals, and the treatment of the gaseous waste stream generates a source of limestone, lime or slaked lime, comprising the steps: (a) admixing carbon dioxide with the source of limestone, lime or slaked lime and water so as to carbonate the limestone, lime or slaked lime, whereby a carbonated sorbent is produced; and (b) contacting the gaseous waste stream containing SO_x and trace metals with the carbonated sorbent, so as to remove SO_x and trace metals from the gaseous waste stream. The water may additionally contain at least one substance selected from the group consisting of surfactants and modifiers. The gaseous waste stream containing SO_x and trace metals may be contacted with the carbonated sorbent in a circulating fluidized bed reactor. The gaseous waste stream may additionally contain NO_x species, and may be contacted with a catalyst adapted to remove the NO_x species following step (b). The flow of clean flue gas containing carbon dioxide may be obtained from contacting the gaseous waste stream with a catalyst adapted to remove NO_x species following step (b).

The present invention also includes, in broadest terms, a system for removing SO_x and trace metals from a gaseous waste stream from coal combustion, whereby the coal combustion generates an untreated gaseous waste stream containing SO_x and trace metals, and the treatment of the gaseous waste stream generates a source of limestone, lime or slaked lime and a flow of clean flue gas containing carbon dioxide, comprising: (a) a coal-burning facility producing a source of an untreated gaseous waste stream containing SO_x and trace

metals, and a apparatus for removing SO_x so as to generate a source of limestone, lime or slaked lime; (b) a carbonation reaction container for admixing the flow of said clean flue gas containing carbon dioxide with the source of limestone, lime or slaked lime with and water so as to carbonate said limestone, lime or slaked lime, thereby producing a carbonated sorbent; 5 (c) a dryer adapted to remove water from the carbonated sorbent; and (d) a sorbent reaction container for contacting the gaseous waste stream containing SO_x and trace metals with the carbonated sorbent, so as to remove SO_x and trace metals from the gaseous waste stream.

The apparatus for removing SO_x may be selected from the group consisting of wet, dry and wet-dry scrubbers. The system may additionally comprise a catalytic reaction 10 container for contacting the gaseous waste stream with a catalyst adapted to remove NO_x species following treatment in the sorbent reaction container. The catalytic reaction container may comprise a selective catalytic reduction catalyst. The system may additionally comprise a conduit adapted to conduct a flow of clean flue gas from the sorbent reaction container to the carbonation reaction container. The system may also comprise a conduit adapted to 15 conduct a flow of clean flue gas from the catalytic reaction container to the carbonation reaction container.

The system may additionally comprise a conduit adapted to conduct the source of limestone, lime or slaked lime from the coal-burning facility to the carbonation reaction container. The system may also comprise a conduit adapted to conduct the untreated gaseous 20 waste stream from the coal-burning facility to the sorbent reaction container. The system may contain a conduit adapted to conduct a flow of water to the carbonation reaction container. The system may include at least one particle separator, and may include a heat exchanger adapted to supply heat from the flow of clean flue gas to the dryer. The sorbent reaction container may also comprise a circulating fluidized bed reactor.

The present invention also includes, in broadest terms, a method of preparing a sorbent from limestone, lime or slaked lime generated from the removal of SO_x from a gaseous waste stream from coal combustion, comprising the steps: obtaining said limestone, lime or slaked lime; and (b) admixing carbon dioxide and water with the limestone, lime or slaked lime so as to carbonate the limestone, lime or slaked lime, thereby producing a carbonated sorbent.

Brief Description of the Drawings

Figure 1 shows the hydration reactivation of spent sorbent in accordance with one embodiment of the present invention.

Figure 2 shows the carbonation reactivation of spent sorbent in accordance with one embodiment of the present invention.

Figure 3 is a schematic of a process of the present invention for combined SO_x/NO_x removal in accordance with one embodiment of the present invention.

Detailed Description of the Preferred Embodiment(s)

In accordance with the foregoing summary, the following presents a detailed description of the preferred embodiment of the invention that is currently considered to be the best mode.

The method of the present invention may be used as a combined SO_x/NO_x removal system, utilizing coal by-products. This method of the present invention for reactivating the partially utilized sorbent is based on a suspension-based carbonation process. The process involves converting the unreacted CaO into calcium carbonate (CaCO_3), as shown in Figure 2, instead of calcium hydroxide (Ca(OH)_2), as shown in Figure 1. Figure 1 shows a partially sulfated CaO particle 4. Water may seep through the CaSO_4 layer 5 to react with the

unsulfated CaO and form high molar volume Ca(OH)₂. The formation of high molar volume Ca(OH)₂ may lead to the development of cracks in the CaSO₄ layer 6. Figure 2 shows the introduction of CO₂ to the Ca(OH)₂ particle, which may then react to produce the desired CaCO₃ 7. Combined with reactivation of unreacted CaO, this process may also provide a 5 better distribution/exposure of available calcium than the reactivated spent sorbent from hydration alone.

The process flow diagram with accompanying control devices is shown in a schematic given in Figure 3. Part of the dry FGD product and ash 25 from the bag-house is sent to a slurry bubble column 15 (carbonator) for hydration and carbonation. A side stream from the 10 clean/scrubbed flue gas 24 may be used to provide CO₂ for carbonation of the ash. A water inlet 34 is provided. Following carbonation, the slurry is sent to a continuous filtration unit 16 to reduce the water content to 35%. Remaining water in the reactivated ash is removed in a continuous powder dryer 17. Water from the continuous filtration unit may be cycled through the system or neutralized by addition of dilute alkaline solutions. The effluent water may also 15 be reused as a wetting agent for the wet-dry scrubber or discharged to the sanitary sewer 23.

Reactivated ash with less than 2% moisture content may then be stored for later use in the reactivated ash storage container 18. This reactivated ash, possibly along with limestone from the contingent limestone storage container 19, is introduced into the fluidized-bed reactor 8 as makeup sorbent along with flue gas from the flue gas inlet 22 and recycled solids 20 from the primary particle separator 9 and the secondary particle separator 10, which pass the ash to the primary ash storage hopper 20 and secondary ash storage hopper 21 respectively. Ash from the storage hoppers may be used in the ash recycle 26 or passed to the ash disposal 27. Hot gases with reduced SO_x levels leaving the Riser reactor are heat-exchanged with wet reactivated ash in a powder dryer unit 11 and pass through another particle separator 12 prior

to entering into the SCR reactor 13. Ammonia is introduced 32 upstream of the SCR reactor to ensure effective mixing. An SCR bypass 31 is also provided. The SCR reactor is designed as a staged fixed-bed reactor with provision for aggressive soot blowing, with 28 as the inlet and 33 as the outlet. Staging of the catalyst bed is considered necessary to reduce the overall 5 pressure drop and to facilitate effective soot blowing. Gases coming out of the SCR reactor pass through the air heater 14, and through the clean flue gas outlet 30 and are redirected into the main breaching of the power plant and carried into the low-temperature wet-dry scrubber 33. An air inlet 29 is provided for the air heater, and the hot air passing from the air heater is passed on to the powder dryer 17. The overall design of the process is modular with inherent 10 flexibility to suit any operating conditions at operator's discretion.

Discussion of Results

Selective Catalytic Reduction (SCR) technology involves the catalytic reaction of ammonia that is injected into the flue gas containing NO_x to produce nitrogen. Specifically, hot flue gases leaving the economizer section of the combustor may be directed into a 15 catalytic reactor. Prior to entering the reactor, ammonia may be injected into the gas stream. Currently, most of the commercial formulations of SCR catalyst comprise vanadia (V_2O_5) as the active material deposited on or incorporated with a substrate (TiO_2). The quantity of ammonia injection may be regulated to provide optimum operation of the reactor at a temperature of 375°C with minimum ammonia slippage (less than 5 ppm).

20 Ca-based sorbents, particularly quicklime (CaO), limestone (CaCO_3) and hydrated lime (Ca(OH)_2), are used extensively in FGD processes in coal-fired combustors. Currently they all suffer from low reactivity and sorbent under-utilization. Typically, because of pore blocking and pore mouth plugging, less than 70% of the available calcium is converted to high molar volume calcium sulfate product. As a consequence, the spent sorbent from a

typical FGD process contains significant amounts of unused sorbent which, unless treated, is disposed of as a solid waste. This in turn may lead to increased costs associated with sorbent disposal and need for fresh sorbent. The spent sorbent exhibits negligible reactivity towards SO₂ unless reactivated to expose the unreacted CaO. Reactivation of the under-utilized 5 sorbent may necessarily require re-exposing and/or redistribution of the CaO from the interior of the sorbent particle and reactivation of the sintered CaO by converting it into a more reactive form. The fundamental challenge and goal of the reactivation process may be to redistribute the CaSO₄ that is located predominantly on the surface of the particle to a more uniform distribution.

10 One of the methods for reactivating partially utilized sorbents is hydration. In this process, the unsulfated CaO is reacted with water to form Ca(OH)₂. Due to the higher molar volume of the hydroxide (33 cc/gmol), compared to CaO (17 cc/gmol), the sorbent particle may expand and the non-porous CaSO₄ shell crack, thereby exposing the hydrate. Reactivation of spent lime/limestone samples from circulating fluidized bed combustor via 15 hydration may cause particle expansion with an increase in internal volume. Moreover, once this reactivated sorbent is reintroduced into the combustor, calcination of the Ca(OH)₂ may further increase the porosity and provide added exposure of CaO to SO₂. Hydration has been known to increase the utilization of spent sorbent from 35% up to 70%. The above mentioned mechanisms for reactivation of spent sorbent via hydration suggest that big particles may 20 undergo reactivation by particle expansion and subsequently develop cracks on the outer inactive sulfate shell. Reactivation of particles that are of smaller dimension might be due to reactions between silica/alumina species and calcium leading to the formation of Ca-Si-Al hydrated complexes. These complexes have high surface areas and may be highly effective for gas-solid reactions.

Reduction of NO_x emissions may be carried out by various means. Modifications or retrofitting during combustion may reduce NO_x generation and subsequent emissions by as much as 40%. Combustion modifications may be limited to simply installing an oxygen meter and reducing the use of excess air; or they may incorporate a more capital-intensive 5 initiative by installing low NO_x burners that may require extensive modification to the furnace and may not be economically suitable for small or older units.

Post-Combustion controls may mean using ammonia with or without a catalyst to remove the NO_x in the flue gases. Reduction without the catalyst may be carried out at higher 10 temperatures and may suffer from some serious drawbacks. Reduction in the presence of catalyst or selective catalytic reduction is fast becoming a method of choice for reducing post-combustion NO_x. This process technology may be applied to a wide range of coal, oil, and gas fired boilers with demonstrated success in achieving greater than 90% NO_x reduction.

Slip of ammonia is a concern in the application of SCR to a coal-fired combustor as it leads to the formation of ammonium bisulfate (NH₄HSO₄) which may cause severe corrosion 15 problems as it condenses on the downstream equipment. The formation of NH₄HSO₄ may be directly related to the sulfur content of the coal used. Combustion of high-sulfur coal may lead to formation of higher flue gas SO₂ content, which might cause more SO₂ to be converted to SO₃ in the SCR reactor thereby aggravating the NH₄HSO₄ problems. For effective application of SCR technology, it may be important for the SO₂ content of the flue 20 gas to be substantially lowered upstream of the SCR reactor.

Utility coal-fired boilers that have low-temperature FGD (wet or wet-dry scrubbers) processes for reduction of SO₂ emission but are non-compliant for NO_x emission face a daunting task in controlling the NO_x emission while continuing the use of high-sulfur coal. A possible strategy for control of NO_x emissions for such units is integration of

post-combustion SO₂ control and SCR technology. The inventive process provides a sorbent that may be used for reduction in SO₂ levels upstream of SCR reactor.

One of the environmentally responsible, yet profitable alternatives for dry FGD product usage is in construction industry. Strength, permeability, and stiffness determinations 5 were made for several FGD materials. The values obtained were compared with the engineering properties of conventional construction materials.

The effectiveness of the inventive ash reactivation process and a comparison of the process with hydration reactivation process was established after conducting extensive studies in a bench-scale set-up with two in-house generated spent sorbents and two ash 10 samples from a commercial coal combustor.

SCR is already in use overseas at power plants that burn natural gas, oil, and low-sulfur coals; however, the technology has never been fully demonstrated on high-sulfur coals in the U.S. utility market. The Gulf Power Company Plant Crist in Pensacola, Florida was the site of a Clean Coal Technology project sponsored by DOE to demonstrate the use of SCR 15 technology for NO_x reduction. The project demonstrated the use of SCR technology at high and low dust loading of the flue gas to provide a cost-effective means of reducing NO_x emissions from the power plant burning high sulfur coal. In this demonstration project, the SCR facility consisted of three 2.5 MWe equivalent SCR reactors supplied by separate 5,000 scfm flue gas slipstreams and six smaller 0.2 MWe-equivalent SCR reactors. These reactors 20 were calculated to be large enough to provide design data that would allow the SCR reactors to be scaled-up to the commercial size. Removal of over 80% NO_x at ammonia slip well under 5 ppm was demonstrated.

In the present combustion configuration for coal-fired boilers, selective catalytic reduction (SCR) of NO_x may be the most promising technology for achieving the drastic

reduction in NO_x levels mandated by EPA regulations. If the coal used in the facility has high sulfur content, however, it may be imperative that SO_x removal from flue gas be undertaken, possibly at higher temperature, prior to removing the NO_x by SCR. The present invention, with demonstrated bench-scale success in removing SO_x, may be integrated with 5 the SCR technology to effectively reduce the SO_x and NO_x emissions while reducing the FGD.

The SCR technology offers the following benefits: it may be one of the few NO_x technologies capable of removing high levels of 80% or more; it may be applicable to all types of boilers, including cyclone-fired boilers which cannot be easily retrofitted with other 10 types of NO_x control technologies; and it may be used with both new and existing power plants. The demonstration of SCR technology may be designed to address several uncertainties, including potential catalyst deactivation due to poisoning by trace metal species, performance of the technology in the presence of high amounts of SO_x, and performance of the SCR catalyst under typical high sulfur coal operating conditions.

15 The presence of arsenic and other trace element species may be detrimental to the performance of SCR catalyst and is known to cause catalyst deactivation and reduced life. Calcium-based sorbents have shown good results for capture of trace metallic species. Calcium oxide may react with both selenium and arsenic to form calcium selenite and arsenate respectively, and thus can be effectively used as a sorbent for these two trace species 20 at medium temperatures (400-600°C). Experimental results by other researchers have shown calcium-based sorbents to be ineffective in lead, cadmium, arsenic, and selenium removal from flue gas stream at temperatures in the range of 500-800°C.

The operation of the inventive desulfurization process upstream of the SCR reactor may not only lower the SO₂ levels in the flue gas stream, but preserve the SCR catalyst by effectively reducing the trace metal loading of the flue gas.

Although most of the inorganic matter in coal remains in the ash, coal combustion does lead to volatilization of some of the low-boiling trace elements and their subsequent transfer into the gas-phase. Some high volatility trace elements are exclusively emitted as vapor through the stack. Some of the less volatile trace elements partly deposit on the ash particles or condense as aerosol particles as the flue gas cools down and are partly emitted into the atmosphere as vapor and particulates. These elements are known as chalcophiles.

10 As, Se, Pb, Sb, and Cd are some examples of elements that display such behavior.

Most of the chalcophilic elements have been identified as air toxics from coal-fired combustor and utility boilers in the 1990 Clean Air Act Amendments (CAAA), and are also considered potential SCR catalyst poisons. The U.S. EPA has been conducting extensive research to determine their health and environmental effects. The control of chalcophilic 15 emissions presents a formidable technical and economical challenge to the operation of coal-fired boilers. This is due in part to the lack of understanding of the behavior of these elements and also due to the fact that they exist in only trace amounts. Considerable effort has been made in last 4-5 years to determine the speciation of these elements. Most of the research has concentrated on determining the exact chemical form(s) of these elements in a 20 highly varied and heterogeneous flue gas environment, with very limited attention being focused on the actual methodology to be applied to their control. Application of sorbents, especially calcium-based sorbents, has shown considerable promise in irreversibly capturing some of these trace species.

Methods and Materials

The following process equipment description represents the primary component systems of the inventive SO_x/NO_x process. There may be considerable system integration with the scrubber unit or existing site equipment that could also be utilized.

Riser Reactor for SO_x Control: At high SO₂ levels the catalyst in the SCR reactor may 5 oxidize SO₂ to SO₃ which would react with ammonia to give ammonium bisulfate. Therefore, it may be important to remove or lower the levels of SO₂ prior to end the gas to the SCR unit. The SO_x reactor may be a fluid-bed riser reactor. The hot flue gas stream generated during 10 coal combustion may be introduced from the bottom of the riser part of the reactor to reduce the SO₂ levels by reacting with reactivated ash sorbent upstream of the SCR reactor. The riser reactor may be designed to provide average solid hold-up of 10%. superficial gas velocities sufficient for fluidization (3-4 m/s), and optimum mixing and retention times. Sample ports may be added at the key locations to test for NO_x, SO_x, and toxin concentration. Inlet and outlet compositions of the gas stream may be monitored continuously for purposes of documenting the performance of the reactor and the reactivated sorbent.

15 *SCR Reactor:* Ammonia may be injected into the gas stream at a sufficient distance upstream of the SCR reactor to allow optimum time for complete mixing. The NO_x reactor may be a staged fixed-bed reactor, with plates of catalyst spaced preferably at equal distances of 0.5 inches. The flue gas stream may enter the reactor at a temperature of 375°C. The reactor may be equipped with soot-blowing accessories in the form of lances placed between 20 the catalyst plates. Currently, most commercial formulations of the SCR catalyst use vanadia (V₂O₅) as the active material deposited on or incorporated with a substrate (TiO₂). The quantity of ammonia injection may be regulated to provide optimum operation of the reactor at a temperature of 375°C with minimum ammonia slippage (less than 5 ppm). The presence of SO_x riser reactor with calcium based sorbent upstream of the SCR reactor may enhance the

performance of the catalyst by removing the presence of trace heavy metals which are considered to be poisonous to the catalyst.

Slurry Bubble Column (Carbonator): Reactivation of the dry scrubber products and ash may be carried out in a slurry bubble column at ambient temperatures. A side stream of 5 clean flue gas may be used to provide CO₂ for carbonation and agitation. The slurry bubble reactor may be designed to operate with a solids concentration of 10%. The carbonation reactivation of the partially used sorbent and ash may result in the re-exposure and redistribution of the unreacted/unutilized calcium sorbents for further reaction with SO₂. Continuous monitoring of the slurry pH and temperature may then be carried out to determine 10 the efficiency of the carbonation reactivation process.

Continuous Filtration and Powder Drying: Following the carbonation reactivation, the slurry may be decanted for filtration prior to sending the filter cake for drying. The drying of the filter cake may be accomplished by contact with the hot gases leaving the fluidized bed reactor. The design of the continuous powder drying may be such that the gas stream leaving 15 the dryer for the SCR reactor is maintained at 400°C. The water from the clarifier may be reused in the carbonator or may be neutralized prior to discharge.

Control and Analytical Instrumentation: Flue gases from the overall process may be closely monitored using a Continuous Emissions Monitor (CEM). Gas composition may be determined on a continual basis upstream of the SO_x reactor and downstream of the SCR 20 reactor. An online ammonia analyzer may be placed downstream of the SCR reactor to closely monitor ammonia slippage and to determine catalyst activity. The ammonia delivery system may be equipped with fail-safe control system to terminate the injection of ammonia into the gas stream if the injected flow rate increases past a pre-determined value. The design

of the system may provide for gas sampling and temperature monitoring at various key locations.

The preferred embodiments herein disclosed are not intended to be exhaustive or to unnecessarily limit the scope of the invention. The preferred embodiments were chosen and 5 described in order to explain the principles of the present invention so that others skilled in the art may practice the invention. Having shown and described preferred embodiments of the present invention, it will be within the ability of one of ordinary skill in the art to make alterations or modifications to the present invention, such as through the substitution of equivalent materials or structural arrangements, or through the use of equivalent process 10 steps, so as to be able to practice the present invention without departing from its spirit as reflected in the appended claims, the text and teaching of which are hereby incorporated by reference herein. It is the intention, therefore, to limit the invention only as indicated by the scope of the claims and equivalents thereof.

15 References

1. Agnihotri, R., Chauk, S., Mahuli, S., Fan, L.-S., "Sorbent Reactivation for Enhanced SO₂, Capture Using Novel Carbonation Technique," *Ind Eng. Chem. Res.*, 1999, 38.
2. Al-Shawabkeh, A., Matsuda, H., Hasatani, M., *AIChE J.*, 1997, 43(1), 173 -179.
3. Bobman, M. H., Weber, G. F., Keener, T. C., "Additive Enhancement of 20 Pressure-Hydrated Lime for Control Of SO₂/NO_x Emissions", presented at the Spring National Meeting of AIChE, Houston, TX, 1985.
4. Bortz, S., and Flament, P., *Proceedings: First Joint Symp. on Dry SO₂ and Simultaneous SO₂/NO_x Control Technologies*, Vol. 1, EPA-600/9-85/020a, (NTIS PB85-232353), 1985.

5. Couturier, M. F., Marquis, D. L., Steward, F. R., and Volmerange, Y., *The Canadian Journal of Chemical Engineering*, 1994, 72, 91-97.
6. Davison, R. L., Natusch, D. F. S., Wallace, J. R., and Evans, C. A., *Environ. Sci. Technol.*, 8, 1107-1113, 1974.
- 5 7. Dismukes, E. B., *Fuel Processing Technology*, 39, 403-416, 1994.
8. Germani, M. S., and Zoeller, W. H., *Environ. Sci. Technol.*, 22(9), 1988.
9. Ghosh-Dastidar, A., Mahuli, S., Agnihotri, R., Fan, L.-S., *Ind. Eng. Chem. Res.*, 1996, 35(2), 598.
10. Ghosh-Dastidar, A., Mahuli, S., Agnihotri, R., and Fan, L.-S., *Environ. Sci. Technol.*, 30, 447-452, 1996.
11. Gregg, S. J., and Sing, K. S. W., "Adsorption, Surface Area and Porosity," Academic Press, 1982.
12. Gullett, B. K., and Raghunathan, K., *Energy and Fuels*, 8, 1068-1076, 1994.
13. Gullett, B. K., Bruce, K. R., *AIChE J.*, 1987, 33, 1719.
- 15 14. Gullett, B. K., Jozewicz, W., and Stefanski, L. A., *Ind. Eng. Chem. Res.*, 31(11), 1992.
15. Ho, T. C., Lee, H. T., Chu, H. W., and Hopper, I R., Proceedings of EERC Workshop on Trace Elements Transformations in Coal-fired Power Systems Workshop, Scottsdale, AZ, April 19-21, 1993.
- 20 16. Ho, T. C., R. Ramanarayanan, I R. Hopper, W. D. Bostick and D. P. Hoffmann, Fluidization VIII, International Symposium of the Engineering Foundation, May 14-19, Tours, France, 1995.
17. Hurst, T. B., Bielawski, G. T., "Dry Scrubber Demonstration Plant," in Proceedings: Symposium on Flue Gas Desulfurization, Volume 2, EPA-600/9-81-019b (NTIS PB81-243164), 1981.

18. Josewicz, W., Chang, I C. S., Bma. T. G., Sedman, C. B.. *Environ. Sci. Technol.*. 1987, 21, 664-670.

19. Josewicz, W., Rochelle, G. T., *Environmental Progress*, 1986, 5(4), 219-224.

20. Jozewicz, W., and B. K. Gullett. *Ind Eng. Chem. Res.* 34(2), 607-612. 1995.

5 21. Khan, T., Kulvarlainen, R., Lee, Y. Y., Fluidized Bed Combustion-Volume 2. ASME, 1995.

22. Mahuli, S., Agnihotri, R., Chauk, S., Ghosh-Dastidar, A., Wei, S.-H., Fan, L.-S.. *AIChE J.* 1997, 43(9), 2323-2335.

23. Markowski, G. R., and Filby, R.. *Env. Sci. Tech.*. 19(9), 1985.

10 24. Marquis, D. L., "Reactivation of Spent CFB Limestone by Hydration," M. Sc. Thesis, University of New Brunswick, Fredericton, NB, 1992.

25. Martinez, J. C., Izquierdo, J. F., Cunill, F., Tejero, J., Querol, J., *Ind. Eng. Chem. Res.*, 1991, 30, 2143-2147.

26. Melia, M. T., McKibben, R. S., Pelsor, B. W., "Utility Flue Gas Desulfurization Survey 15 July 1982-March 1983." Project Summary, EPRI Contract No. RP982-32. EPRI. 1983.

27. Natusch D. F. S.. Wallace J. R. and Evans C. A., *Science*. 183, 202. 1974.

28. Ondov, J. M., Ragaini, R. C., and Biermann, A. H., *Env. Sci. Tech.*. 13(8). 946-953, 1979.

29. Owens, W. D., Sarofim, A.F., and Pershing, D.W., Proc. of Trace Elements Transformations in Coal-fired Power Systems Workshop, Scottsdale, AZ. April 19-21, 1993.

20 30. Palazzolo, M. A.. Bma. T. G., Kelly, M. E., "Current Status of Dry SO₂ Control System," in Proceedings: Eighth EPA/EPRI Symposium on Flue Gas Desulfurization, Volume 2, EPA-600/9-84-017b (NTIS PB84-223049), 1984.

31. Parson E. L. Jr., Hemenway L. F., Kragh, O. T., Bma, T. G., Ostop, R. L., "SO₂ Removal in Dry FGD," in Proceedings: Symposium on Flue Gas Desulfurization, Volume 2. EPA-600/9-81-019b (NTIS PB81-243164), 1981.

32. Perry, R.H., and Green, D., Chemical Engineers Handbook. 6th Ed., McGraw Hill. 1984.

5 33. Shearer, J. A., Smith, G. W., Myles, K. M., Johnson, I., *J Air Pollut. Control Assoc.*, 1980, 30, 684-688.

34. Thurnau, R. C., and Fournier D. Jr., *J Air Waste Manage. Assoc.*, 42(2), 179-184, 1992.

35. Uberoi, M.. and Shadman, F., *Environ. Sci. Technol.*, 25(7), 1991.

36. Uberoi, M.. and Shadman, F., *AIChE J.*, 36(2), 1990.

10 37. Wei, S.-H., Mahuli, S. K., Agnihotri, R., Fan, L.-S.. *Ind Eng. Chem. Res.*, 1997, 36, 2141-2148.

38. Wouterlood, H. J., and Bowling, K. M., *Environ. Sci. Technol.*, 13(1), 93-97, 1979

39. Wu, B., Jaanu, K. K., and Shadman, F., *Environ. Sci. Technol.*, 1660-1665

The foregoing references are hereby incorporated herein by reference.

What is claimed is:

Reactivation Of Coal Combustion Generated Limestone, Lime Or Slaked Lime Using CO₂

1. A method of removing SO_x and trace metals from a gaseous waste stream from coal combustion, said coal combustion generating (a) an untreated gaseous waste stream containing SO_x and trace metals, and the treatment of said gaseous waste stream generating (b) a source of limestone, lime or slaked lime:
 - (a) admixing carbon dioxide with said source of limestone, lime or slaked lime and water so as to carbonate said limestone, lime or slaked lime, so as to produce a carbonated sorbent; and
 - (b) contacting said gaseous waste stream containing SO_x and trace metals with said carbonated sorbent, so as to remove SO_x and trace metals from said gaseous waste stream.
2. A method according to claim 1 wherein said water additionally contains at least one substance selected from the group consisting of surfactants and modifiers.
3. A method according to claim 1 wherein said gaseous waste stream containing SO_x and trace metals is contacted with said carbonated sorbent in a circulating fluidized bed reactor.
4. A method according to claim 1 wherein said gaseous waste stream contains NO_x species, and said gaseous waste stream is contacted with a catalyst adapted to remove said NO_x species following step (b).

20 Reactivation Of Coal Combustion Generated Limestone, Lime Or Slaked Lime Using Clean Flue Gas as Source of CO₂

5. A method of removing SO_x and trace metals from a gaseous waste stream from coal combustion, said coal combustion generating (a) an untreated gaseous waste stream containing SO_x and trace metals, and the treatment of said gaseous waste stream

generating (b) a source of limestone, lime or slaked lime and (c) a flow of clean flue gas containing carbon dioxide, said method comprising the steps:

- (a) admixing said flow of said clean flue gas containing carbon dioxide with said source of limestone, lime or slaked lime and water so as to carbonate said limestone, lime or slaked lime, so as to produce a carbonated sorbent; and
- 5 (b) contacting said gaseous waste stream containing SO_x and trace metals with said carbonated sorbent, so as to remove SO_x and trace metals from said gaseous waste stream.
6. A method according to claim 5 wherein said water additionally contains at least one substance selected from the group consisting of surfactants and modifiers.
- 10 7. A method according to claim 5 wherein said gaseous waste stream containing SO_x and trace metals is contacted with said carbonated sorbent in a circulating fluidized bed reactor.
8. A method according to claim 5 wherein said gaseous waste stream contains NO_x species, and said gaseous waste stream is contacted with a catalyst adapted to remove said NO_x species following step (b).
- 15 9. A method according to claim 8 wherein said flow of clean flue gas containing carbon dioxide is obtained from contacting said gaseous waste stream with a catalyst adapted to remove NO_x species following step (b).

System for Reactivation Of Coal Combustion Generated Limestone, Lime Or Slaked Lime

20 Using Clean Flue Gas as Source of CO_2

10. A system for removing SO_x and trace metals from a gaseous waste stream from coal combustion, said coal combustion generating (a) an untreated gaseous waste stream containing SO_x and trace metals, and the treatment of said gaseous waste stream

generating (b) a source of limestone, lime or slaked lime and (c) a flow of clean flue gas containing carbon dioxide, said system comprising:

- (a) a coal-burning facility producing a source of an untreated gaseous waste stream containing SO_x and trace metals, and a apparatus for removing SO_x so as to generate a source of limestone, lime or slaked lime;
- 5 (b) a carbonation reaction container for admixing said flow of said clean flue gas containing carbon dioxide with said source of limestone, lime or slaked lime with and water so as to carbonate said limestone, lime or slaked lime, so as to produce a carbonated sorbent;
- (c) a dryer adapted to remove water from said a carbonated sorbent; and
- 10 (d) a sorbent reaction container for contacting said gaseous waste stream containing SO_x and trace metals with said carbonated sorbent, so as to remove SO_x and trace metals from said gaseous waste stream.

11. A system according to claim 10 wherein said apparatus for removing SO_x is selected from the group consisting of wet, dry and wet-dry scrubbers.

15 12. A system according to claim 10 additionally comprising a catalytic reaction container for contacting said gaseous waste stream with a catalyst adapted to remove NO_x species following treatment in said sorbent reaction container.

13. A system according to claim 12 wherein said catalytic reaction container comprises a selective catalytic reduction catalyst.

20 14. A system according to claim 10 additionally comprising a conduit adapted to conduct a flow of clean flue gas from said sorbent reaction container to said carbonation reaction container.

15. A system according to claim 12 additionally comprising a conduit adapted to conduct a flow of clean flue gas from said catalytic reaction container to said carbonation reaction container.

16. A system according to claim 10 additionally comprising a conduit adapted to conduct said 5 source of limestone, lime or slaked lime from said coal-burning facility to said carbonation reaction container.

17. A system according to claim 10 additionally comprising a conduit adapted to conduct said untreated gaseous waste stream from said coal-burning facility to said sorbent reaction container.

10 18. A system according to claim 10 additionally comprising a conduit adapted to conduct a flow of water to said carbonation reaction container.

19. A system according to claim 10 additionally comprising at least one particle separator.

20. A system according to claim 10 additionally comprising a heat exchanger adapted to supply heat from said flow of clean flue gas to said dryer.

15 21. A system according to claim 10 wherein said sorbent reaction container comprises a circulating fluidized bed reactor.

Method Of Preparing A Sorbent From Limestone, Lime Or Slaked Lime Generated From The Removal Of SO_x From A Gaseous Waste Stream From Coal Combustion

22. A method of preparing a sorbent from limestone, lime or slaked lime generated from the 20 removal of SO_x from a gaseous waste stream from coal combustion, said method comprising:

(a) obtaining said limestone, lime or slaked lime; and

(b) admixing carbon dioxide and water with said limestone, lime or slaked lime so as to carbonate said limestone, lime or slaked lime, so as to produce a carbonated sorbent.

23. A sorbent produced in accordance with the method of claim 22.

1/2

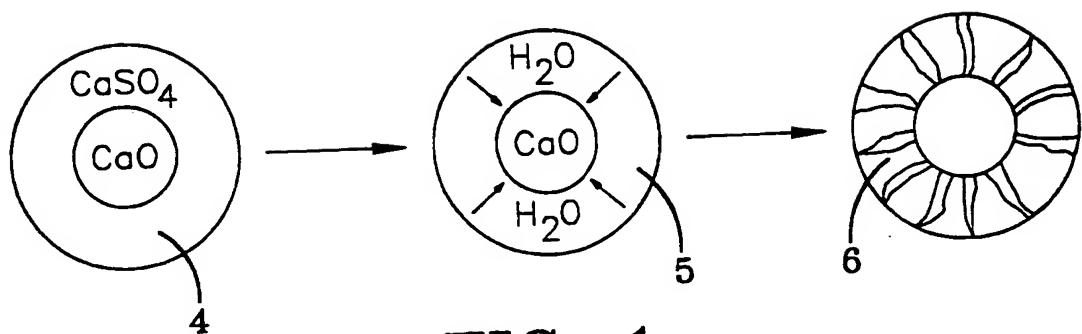


FIG-1

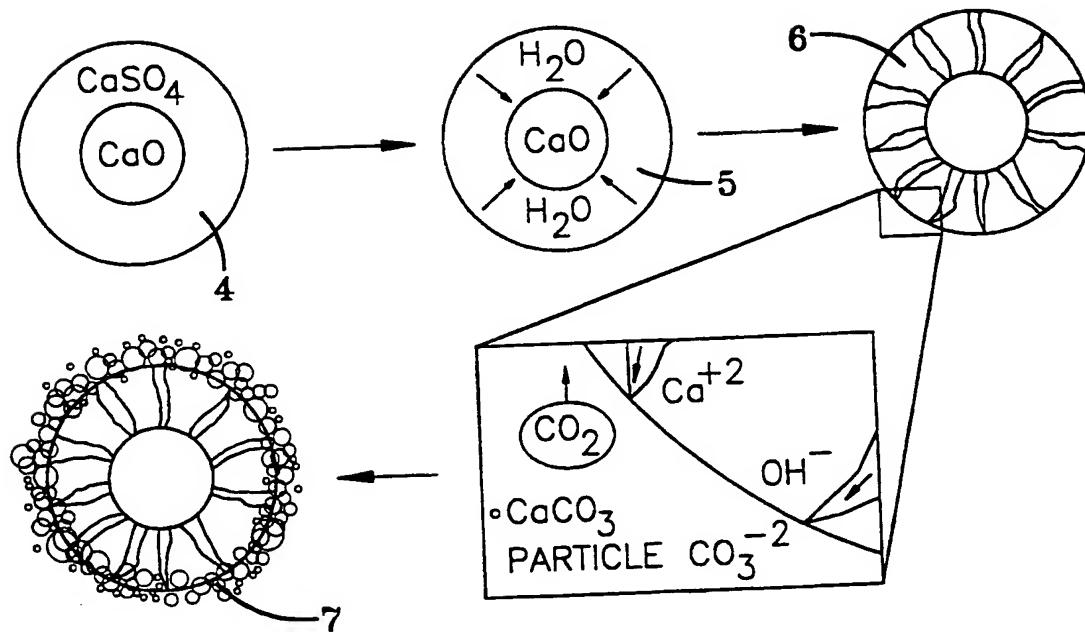


FIG-2

2/2

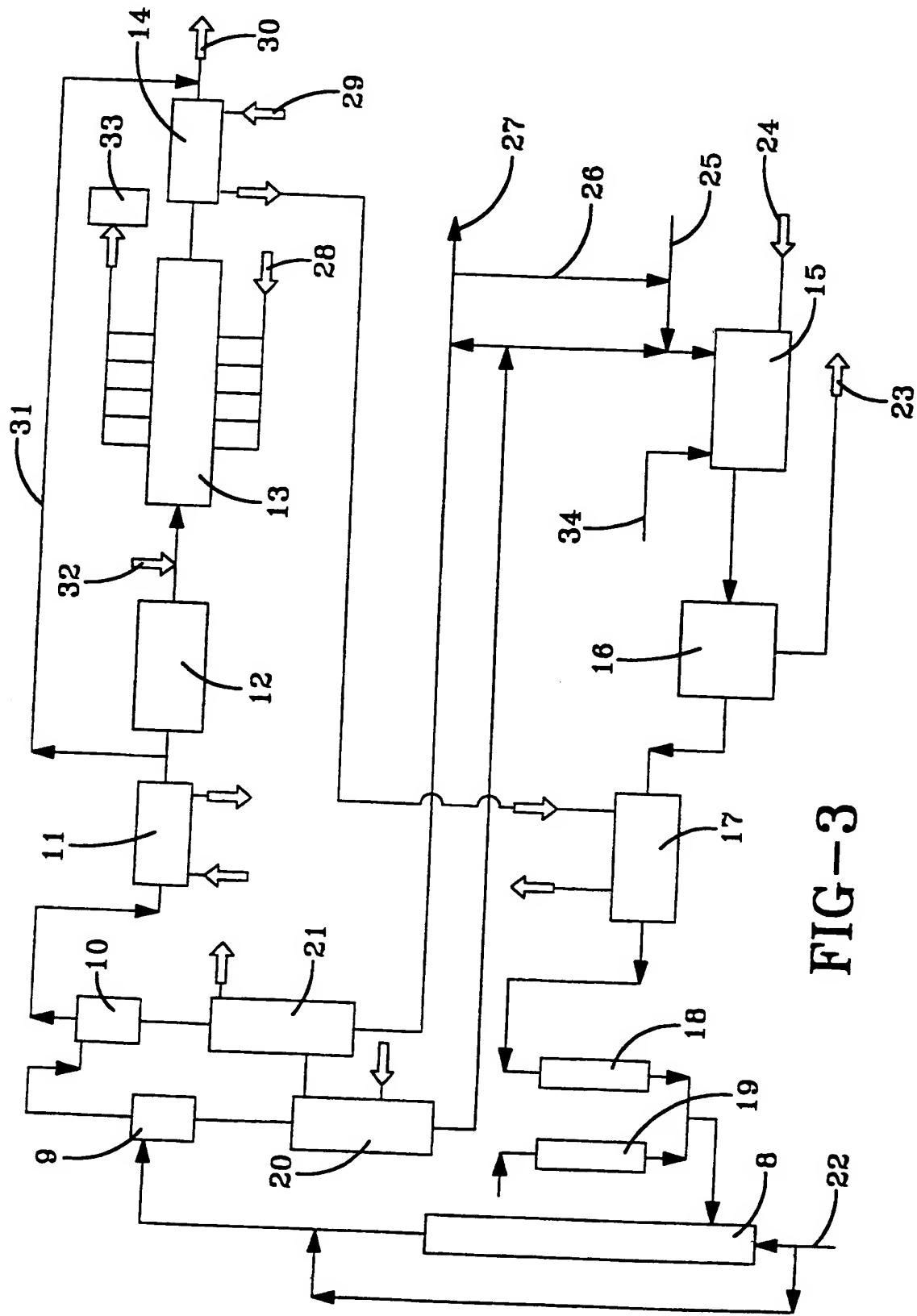


FIG-3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/20518

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :B01D 53/34, 53/50, 53/56, 53/60

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 422/170, 171, 173; 423/210, 239.1, 243.07, 243.08, 635, 636, 637, 640; 502/400

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST

Search terms: SOx, NOx, limestone, lime, slaked lime, carbon dioxide, water, carbonated sorbent

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Agnihotri et al, Sorbent/Ash Reactivation for Enhanced SO ₂ Capture Using a Novel Carbonation Technique, Ind. Eng. Chem. Res. 38, pages 812-819, 1/1999	1-3, 5-7, 22-23
Y	Agnihotri et al, Mechanism of Arsenic Sorption by Hydrated Lime, Environ. Sci. Technol. 1997, Vol. 31, No. 11, pages 3226-3231.	4, 8-21
Y		1-23

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"		document defining the general state of the art which is not considered to be of particular relevance
"E"	"X"	earlier document published on or after the international filing date
"L"		document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	"Y"	document referring to an oral disclosure, use, exhibition or other means
"P"	"&"	document published prior to the international filing date but later than the priority date claimed

Date of the actual completion of the international search

13 OCTOBER 2000

Date of mailing of the international search report

14 NOV 2000

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized Officer

HIEN TRAN

Telephone No. (703) 308-0661

DEBORAH THOMAS
PARALEGA

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/20518

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

422/170, 171, 173; 423/210, 239.1, 243.07, 243.08, 635, 636, 637; 502/400

